

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Manufacture of Hydrogen Peroxide

5 We, LAPORTE CHEMICALS LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to an improved process for the manufacture of hydrogen peroxide by the alternate reduction and oxidation of organic compounds.

15 It is well-known that hydrogen peroxide can be manufactured by a process employing the oxidation of certain organic compounds, thus, for example United Kingdom Specification No. 465,070 describes a process for the production of hydrogen peroxide in which an alkylated anthraquinone is hydrogenated in a solvent by means of hydrogen in the presence of a catalyst, to the corresponding alkylated quinol which, after separation from the catalyst, is oxidised with oxygen to produce hydrogen peroxide with regeneration of the alkylated anthraquinone. Such a process is thus 25 cyclic as the alkylated anthraquinone is re-cycled to the hydrogenation stage after the removal of the hydrogen peroxide by aqueous extraction.

30 It is an object of this invention to provide improvements in the aqueous extraction stage of the process in the production of hydrogen peroxide by the cyclic reduction and oxidation of organic compounds.

35 It has now been found, according to this invention, that improved results can be obtained in the aqueous extraction stage of such a process by using an inorganic hydrogen peroxide stabiliser dissolved in the water used for the aqueous extraction.

40 Accordingly, the present invention provides in a cyclic process for the manufacture of hydrogen peroxide involving the alternate oxidation and reduction of an organic compound in a non-aqueous solvent medium with extrac-

tion of the hydrogen peroxide formed from the solvent medium by means of an aqueous liquid, the step of using an aqueous liquid having dissolved therein an inorganic hydrogen peroxide stabiliser.

50 Preferably the inorganic stabiliser is an alkali metal phosphate for example an alkali metal metaphosphate, pyrophosphate, or polyphosphate. The preferred stabiliser is normal sodium pyrophosphate or disodium dihydrogen pyrophosphate.

55 The stabiliser is preferably used in quantities varying from 0.01 to 0.5 grams/litre of water used in the extraction.

60 In the manufacture of hydrogen peroxide by a cyclic autoxidation method, the resultant hydrogen peroxide from the aqueous extraction stage always contains some organic compounds. Thus, the hydrogen peroxide is saturated with the solvents used in the cyclic process, and it may also contain traces of the organic intermediate used. In addition to this, the aqueous hydrogen peroxide will also contain other substances formed by the degradation of the solvent or organic intermediate. The presence of these other compounds may be indicated, for example, by the acidity of the hydrogen peroxide, or by its "non-volatile carbon content". When the extracted hydrogen peroxide is distilled with fractionation *in vacuo*, the dissolved solvents, if normally steam-volatile, are largely recovered in the overhead product, but the degradation compounds appear largely in the fractionated product, or remain in the boiler residue—hence the expression "non-volatile carbon". 70 75 80

85 Serious disadvantages can result from the presence of these organic degradation compounds in the crude aqueous extract. Thus, organic compounds which are concentrated in solution in aqueous hydrogen peroxide in the boiler of a distillation process, can form explosive mixtures, while the presence of carbon in the distilled final product is undesirable for

some purposes. It is therefore necessary to minimise the quantity of organic compounds in the resultant hydrogen peroxide.

5 It has been shown that degradation of the organic compounds occurs particularly in the aqueous phase because of oxidation of the dissolved solvents by hydrogen peroxide. It has also been found that the rate of this oxidation is increased by the presence of those cations which cause decomposition of hydrogen peroxide.

10 It has now been found that this degradation caused by oxidation can be largely eliminated, if an inorganic hydrogen peroxide stabiliser is present in the aqueous extraction liquid. In this way, it is possible to hinder the formation of those organic compounds which are considered undesirable, during the subsequent distillation of the crude extract hydrogen peroxide.

#### EXAMPLE 1.

100 g. of 2-ethyl anthraquinone in a litre of a mixture of equal volumes of benzene and methyl cyclohexanol acetate was in equilibrium with an aqueous phase of 350 ml. containing 200 g/l of hydrogen peroxide. The solution was kept at 20° C. and samples of the aqueous phase was withdrawn at intervals of time and their acidity determined. In one instance, the equivalent of 0.05 part per million of copper was added in cationic form, and the same acidity determinations made. These tests were then repeated after the addition of 50 parts per million of sodium stannate to the aqueous phase. The results given below show the initial rate of formation of acid as ml. of normal acid/litre/hour. The results show how the addition of sodium stannate prevents formation of acid:—

40 Addition to solution	Rate of formation of acid
None	0.003—0.007
0.05 ppm Cu	0.035
50 ppm Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0
45 50 ppm Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> +	
0.05 ppm Cu	0

#### EXAMPLE 2.

Example 1 was repeated but 50 parts per million of aluminium phosphate were added to the aqueous phase. The results were as follows:—

50 Addition to solution	Rate of formation of acid
None	0.063
55 50 ppm AlPO <sub>4</sub>	0.034

#### EXAMPLE 3.

An autoxidation cycle was operated, using a solution containing 90 g. of 2-ethyl anthraquinone in each litre of a mixture of equal

60 volumes of xylene and methyl cyclohexanol acetate. This solution was cycled continuously through a hydrogenation stage, where the anthraquinone was partially reduced, the quinol concentration being maintained at the equivalent of 3.0—3.5 g/l of hydrogen peroxide. After oxidation, the hydrogen peroxide formed was extracted with water in a conventional counter-current plate column; the concentration of hydrogen peroxide in the aqueous extract was maintained at about 150 70 g/l. The organic solution was then returned to the hydrogenation stage. In one experiment, distilled water containing 20 parts/million of ammonium nitrate as a corrosion inhibitor, was used for the extraction; in another experiment, 75 distilled water containing 20 parts per million of ammonium nitrate and 100 parts per million of sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) was used. The "non-volatile carbon" content of the aqueous hydrogen peroxide was then determined. This was done by measuring the carbon concentration in a sample which had been concentrated under vacuum to 40% of its original volume, the concentration reported being based on the original volume: —

Addition to water	"Non-volatile carbon" content
20 ppm NH <sub>4</sub> NO <sub>3</sub>	0.20 g/l carbon
100 ppm Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> +	
20 ppm NH <sub>4</sub> NO <sub>3</sub>	0.11 g/l carbon

#### EXAMPLE 4.

Example 3 was repeated but the distilled water used for extraction containing 20 parts per million of ammonium nitrate and 84 parts per million of sodium acid pyrophosphate (Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>):—

Addition to water	"Non-volatile carbon" content
20 ppm NH <sub>4</sub> NO <sub>3</sub>	0.20 g/l carbon
84 ppm Na <sub>2</sub> H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> +	
20 ppm NH <sub>4</sub> NO <sub>3</sub>	0.11 g/l carbon

It will be understood that the invention is not confined to hydrogen peroxide extracts obtained with the aid of anthraquinone derivatives but is applicable to those obtained using other compounds which can be used in the autoxidation process such as phenazine and its derivatives.

#### WHAT WE CLAIM IS:—

1. In a cyclic process for the manufacture of hydrogen peroxide involving the alternate oxidation and reduction of an organic compound in a non-aqueous solvent medium with extraction of the hydrogen peroxide formed from the solvent medium by means of an aqueous liquid, the step of using an aqueous liquid 115 having dissolved therein an inorganic hydrogen peroxide stabiliser.

2. A process according to Claim 1 wherein

the inorganic stabiliser is an alkali metal phosphate for example an alkali metal metaphosphate, pyrophosphate or polyphosphate.

3. A process according to Claim 2 wherein the stabiliser is normal sodium pyrophosphate or disodium dihydrogen pyrophosphate.

4. A process according to any one of the preceding claims wherein the stabiliser is used in a quantity of from 0.01 to 0.5 gms/litre of water used in the extraction.

5. A process for the manufacture of hydrogen peroxide according to Claim 1 substanti-

ally as described with reference to any one of the examples.

6. Hydrogen peroxide when manufactured by the process claimed in any one of the preceding claims.

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## PROVISIONAL SPECIFICATION

### Improvements in or relating to the Manufacture of Hydrogen Peroxide

We, LAPORTE CHEMICALS LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, do hereby declare this invention to be described in the following statement:—

This invention relates to an improved process for the manufacture of hydrogen peroxide by the alternate reduction and oxidation of organic compounds.

It is well-known that hydrogen peroxide can be manufactured by a process employing the oxidation of certain organic compounds, thus, for example Specification No. 465,070 describes a process for the production of hydrogen peroxide in which an alkylated anthraquinone is hydrogenated in a solvent by means of hydrogen in the presence of the catalyst, to the corresponding alkylated quinol which, after separation from the catalyst, is oxidised with oxygen to produce hydrogen peroxide with regeneration of the alkylated anthraquinone. Such a process is thus cyclic as the alkylated anthraquinone is recycled to the hydrogenation stage after the removal of the hydrogen peroxide by aqueous extraction.

It is an object of this invention to provide improvements in the aqueous extraction stage of the process in the production of hydrogen peroxide by the cyclic reduction and oxidation of organic compounds.

It has now been found, according to this invention, that improved results can be obtained in the aqueous extraction stage of such a process by using an inorganic hydrogen peroxide stabiliser dissolved in the water used for the aqueous extraction.

Accordingly, the present invention provides in a cyclic process for the manufacture of hydrogen peroxide involving the alternate oxidation and reduction of an organic compound with extraction of the hydrogen peroxide formed by means of an aqueous liquid the step of using an aqueous liquid having dissolved therein an inorganic hydrogen peroxide stabiliser.

Preferably the inorganic stabiliser is an alkali metal phosphate such as a metaphos-

It has now been found that this degradation

phate, a pyrophosphate, or a polyphosphate. The preferred stabiliser is sodium pyrophosphate or acid pyrophosphate.

The stabiliser is preferably used in quantities varying from 0.01 to 0.5 grams/litre of water used in the extraction.

In the manufacture of hydrogen peroxide by a cyclic autoxidation method, the resultant hydrogen peroxide from the aqueous extraction stage always contains some organic compounds. Thus, the hydrogen peroxide is saturated with the solvents used in the cyclic process, and it may also contain traces of the organic intermediate used. In addition to this, the aqueous hydrogen peroxide will also contain other substances formed by the degradation of the solvent or organic intermediate. The presence of these other compounds may be indicated, for example, by the acidity of the hydrogen peroxide, or by its "non-volatile carbon content". When the extracted hydrogen peroxide is distilled with fractionation *in vacuo*, the dissolved solvents, if normally steam-volatile, are largely recovered in the overhead product, but the degradation compounds appear largely in the fractionated product, or remain in the boiler residue—hence the expression "non-volatile carbon".

Serious disadvantages can result from the presence of these organic degradation compounds in the crude aqueous extract. Thus, organic compounds which are concentrated in solution in aqueous hydrogen peroxide in the boiler of a distillation process, can form explosive mixtures, while the presence of carbon in the distilled final product is undesirable for some purposes. It is therefore necessary to minimise the quantity of organic compounds in the resultant hydrogen peroxide.

It has been shown that degradation of the organic compounds occurs particularly in the aqueous phase because of oxidation of the dissolved solvents by hydrogen peroxide. It has also been found that the rate of this oxidation is increased by the presence of those cations which cause decomposition of hydrogen peroxide.

caused by oxidation can be largely eliminated, if an inorganic hydrogen peroxide stabiliser is present in the aqueous extraction liquid. In this way, it is possible to hinder the formation of those organic compounds which are considered undesirable, during the subsequent distillation of the crude extract hydrogen peroxide, by adding an inorganic hydrogen peroxide stabiliser to the water used for aqueous extraction from the organic cycle.

#### EXAMPLES.

1. 100 g. of 2-ethyl anthraquinone in a litre of a mixture of equal volumes of benzene and methyl cyclohexanol acetate was in equilibrium with an aqueous phase of 350 ml. containing 200 g/l of hydrogen peroxide. The solution was kept at 20° C. and samples of the aqueous phase were withdrawn at intervals of time and their acidity determined. In one instance, the equivalent of 0.05 part per million of copper was added in cationic form, and the same acidity determinations made. These tests were then repeated after the addition of 50 parts per million of sodium stannate to the aqueous phase. The results given below show the initial rate of formation of acid as ml of normal acid/litre/hour. The results show how the addition of sodium stannate prevents formation of acid:—

Addition to solution	Rate of formation of acid
None	0.003—0.007
0.05 ppm Cu	0.035
50 ppm $\text{Na}_2\text{SnO}_3$	0
50 ppm $\text{Na}_2\text{SnO}_3$ + 0.05 ppm Cu	0

2. Example 1 was repeated but 50 parts per million of aluminium phosphate were added to the aqueous phase. The results were as follows:—

Addition to solution	Rate of formation of acid
None	0.063
50 ppm $\text{AlPO}_4$	0.034

3. An autoxidation cycle was operated, using a solution containing 90 g. of 2-ethyl anthraquinone in each litre of a mixture of xylene and methyl cyclohexanol acetate. This solution was cycled continuously through a hydrogenation stage, where the anthraquinone was

partially reduced, the quinol concentration being maintained at the equivalent of 3.0—3.5 g/l of hydrogen peroxide. After oxidation, the hydrogen peroxide formed was extracted with water in a conventional counter-current plate column; the concentration of hydrogen peroxide in the aqueous extract was maintained at about 150 g/l. The organic solution was then returned to the hydrogenation stage. In one experiment, distilled water containing 20 parts/million of ammonium nitrate as a corrosion inhibitor, was used for the extraction; in another experiment, distilled water containing 20 parts per million of ammonium nitrate and 100 parts per million of sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) was used. The "non-volatile carbon" content of the aqueous hydrogen peroxide was then determined. This was done by measuring the carbon concentration in a sample which had been concentrated under vacuum to 40% of its original volume, the concentration reported being based on the original volume:—

Addition to water	"Non-volatile carbon" content
20 ppm $\text{NH}_4\text{NO}_3$	0.20 g/l carbon
100 ppm $\text{Na}_4\text{P}_2\text{O}_7$ + 20 ppm $\text{NH}_4\text{NO}_3$	0.11 g/l carbon

4. Example 3 was repeated but the distilled water used for extraction contained 20 parts per million of ammonium nitrate and 84 parts per million of sodium acid pyrophosphate ( $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ):—

Addition to water	"Non-volatile carbon" content
20 ppm $\text{NH}_4\text{NO}_3$	0.20 g/l carbon
84 ppm $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ + 20 ppm $\text{NH}_4\text{NO}_3$	0.11 g/l carbon

It will be understood that the invention is not confined to hydrogen peroxide extracts obtained with the aid of anthraquinone derivatives but is applicable to those obtained using other compounds which can be used in the autoxidation process such as phenazine and its derivatives.

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**Improvements in or relating to the manufacture of hydrogen peroxide**

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**Applicant(s):** LAPORTE CHEMICAL  
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**Abstract of GB 811733 (A)**

In the production of hydrogen peroxide by a process involving alternate reduction and reoxidation of an organic compound in a solvent medium, the hydrogen peroxide produced is extracted from the solvent medium by means of an aqueous solution containing an inorganic hydrogen peroxide stabilizer preferably in an amount of 0.01-0.5 gm/l. Organic compounds specified are 2-ethyl anthraquinone and phenazine. Stabilizers specified are alkali metal metaphosphate, pyrophosphate (e.g. normal sodium pyrophosphate and disodium dihydrogen pyrophosphate), and polyphosphate, aluminium phosphate, and sodium stannate. Ammonium nitrate may be present as corrosion inhibitor. In an example, a solution containing 90 gm/l. of 2-ethyl anthraquinone in a mixture of xylene and methyl cyclohexanyl acetate was subjected to reduction to produce the quinol in an amount corresponding to 3.0-3.5 gm/l. After reoxidation and extraction with water, a solution containing 150 gm/l. of hydrogen peroxide was obtained. Specification 465,070 is referred to.

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